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# AN INVESTIGATION OF THE CATALYTIC ACTIVATION OF MOLECULAR OXYGEN BY SULFONIUM COMPOUNDS

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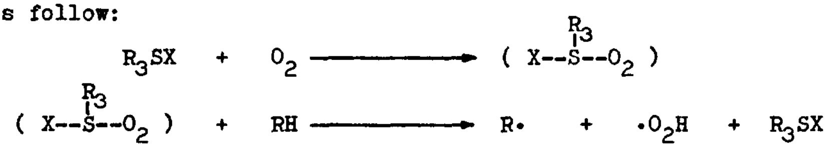
In the previous papers,[1,2] a presumption was made that the distinguished activity of sulfonium compounds in the homogeneous liquid-phase oxidation of hydrocarbons would be ascribed to their catalytic activations of molecular oxygen as follow:



$$R_3SX + O_2 \longrightarrow (X\text{--}\overset{R_3}{S}\text{--}O_2)$$

$$(X\text{--}\overset{R_3}{S}\text{--}O_2) + RH \longrightarrow R\cdot + \cdot O_2H + R_3SX$$

The partially occupied d-orbitals of the central sulfur[3] contribute markedly to this catalytic activation of $O_2$ on the basis of the interaction between the sulfur d-orbitals (especially, $d_{xz}$ or $d_{yz}$) and $1\pi_g$-orbitals of $O_2$.[1] The present study intends to elucidate the above interaction mainly by the ultraviolet absorption measurements. Before discussing regarding the above interaction, it is necessary first to determine the molecular structures of the sulfonium compounds. The ASMO SCF calculations on $(CH_3)_3SCl$ supported the $D_{3h}$ symmetrical sulfonium cation and suggested the suitable location of the counter chlorine (S-Cl=3.5 - 4.5 Å) from the energetic point of view (see Table 1). Secondly, it is worthy of emphasis that molecular oxygen brings about the red shifts of the absorption bands of sulfonium compounds near 200 mμ (5.77 - 6.36 eV) measured in a nitrogen atmosphere. This band near 200 mμ is assigned to be the transition of electrons from the nonbonding sulfur 3p-orbital to the sulfur d-orbitals (5.10 - 6.65 eV) by the ASMO SCF calculations. The above phenomenon relates immediately to the interaction between the sulfonium compounds and molecular oxygen, i.e., the electron-donor property of the former causes the lowering of the energies of the partially occupied sulfur d-orbitals by the interaction of the latter (an electron accepter).[4] As Table 2 indicates, this concept would be persuaded by the parallelism between the range of the red shift ($\Delta\lambda$ in eV) and the catalytic activity of the sulfonium compound (estimated by $R_{max}$).

Table 1. Energy Change in Various Configurations of $(CH_3)_3SCl$.

| ∠CSCl | μ (D) | $E_{HF}$ (eV) | S-Cl (A) | μ (D) | $E_{HF}$ (eV) |
|---|---|---|---|---|---|
| 90° | 13.48 | -782.25 | 4.5 | 19.97 | -798.82 |
| 100° | 14.82 | -771.45 | 3.5 | 13.48 | -782.25 |
| 109°28' | 16.21 | -769.11 | 3.0 | 9.80 | -767.32 |
| | | | 2.5 | 6.30 | -743.77 |

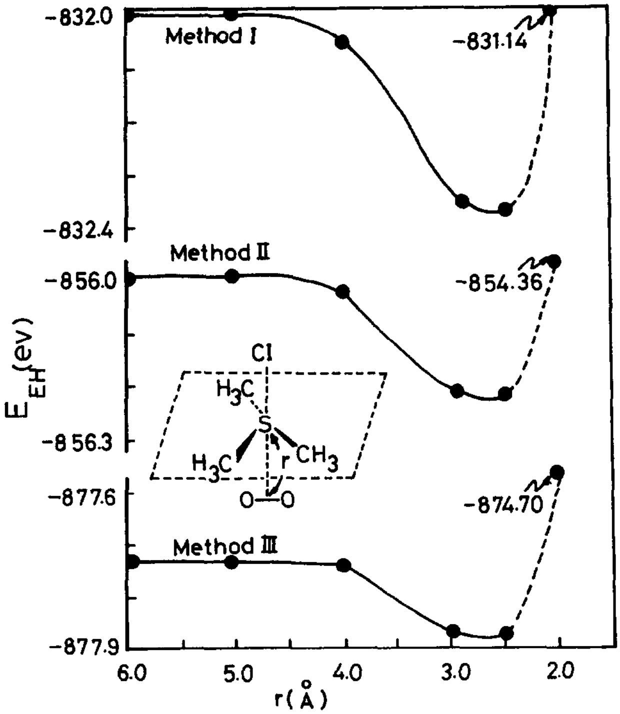


Fig. 1. Energy change in the system of $(CH_3)_3SCl-O_2$. (in Methods I, II, and III, coulomb integrals of O 2p-orbitals were -13.61eV, -15.85 eV, and -13.61eV(S 3p:-17.00eV), respectively. Except Method III, that of S 3p was -13.32eV.)

It is of interest here to estimate the suitable range of the interaction between the sulfonium compound and molecular oxygen. The most possible mode of the interaction of the latter was found to be parallel to the ligand plane of the

Table 2. Ultraviolet Absorption Bands of the System of Sulfonium Compound-$O_2$ in $C_2H_5OH$.

| Sulfonium Compound (Concentration, mol/l × $10^5$) | Temperature ($^oC$) | $^1L_a$ $\lambda_{max}(\log\varepsilon)$ | $S((3p_z)^2 \rightarrow (3p_z)(3d))$ $\lambda_{max}(\log\varepsilon)$ | $\Delta\lambda$ (eV) | $R_{max} \times 10^4$ a) (mol/l sec) |
|---|---|---|---|---|---|
| $(C_6H_5)_3SBF_4$ (6.70) | -40±1 | 227 (4.23) | 214 (4.23) | 0.30 | 1.50 |
| $(C_6H_5)_3SBF_4$ (1.43) | -40±1 | 233 (4.27) | 208 (4.32) | 0.20 | 0.97 |
| $(C_6H_5)_3S\ \frac{1}{3}PO_4$ (1.70) | 4±1 | 235 (4.03) | 210 (4.30) | 0.17 | 1.89 |
| $CH_3S(C_6H_5)_2BF_4$ (2.08) | 0±1 | 232.5(3.99) | 206 (4.32) | 0.12 | 1.10 |
| $CH_3S(C_6H_5)_2ClO_4$(2.00) | 25±1 | 235.5(3.89) | 206 (3.94) | 0.05 | 0.87 |
| n-$C_4H_9S(C_6H_5)_2ClO_4$(1.46) | 25±1 | 234 (4.12) | 206.5(4.35) | 0.07 | 0.92 |
| $(CH_3)_3SBr$ (4.78) | 0±1 | 230 (2.82) | 207.5(3.44) | 0.25 | 1.93 |
| $(C_6H_5)_3SCl$ (1.67) | 25±1 | 227 (4.65) | 209 (4.73) | 0.14 | (1.12) |
| $(C_6H_5)_3SeCl$(1.45)$^{b)}$ | 25±1 |  | 207.5(4.50) | 0.105 | (1.04) |
| $(C_6H_5)_3TeCl$(1.40)$^{b)}$ | 25±1 |  | 208 (4.55) | 0.09 | (0.45) |
| none |  |  |  |  | 0.69 (0.34) |

a) $R_{max}$ and those in parentheses were determined from the amount of $O_2$ absorbed (mol) corresponding to that of hydroperoxides formed (mol) in α-pinene and cumene oxidations at 85°C (Catalyst amount=3.0 mmol/l), respectively.

b) They were listed for the comparison's sake.

$^1L_b$ bands were neglected in this table.

sulfonium cation.[5] Fig. 1 indicates that the interaction occurrs in the range of the distance of $(CH_3)_3SCl-O_2$, 2.5 - 3.0 Å. This range of the interaction suggests the contribution of the specially far-reaching sulfur d-orbitals of the sulfonium compound to the catalytic activation of $O_2$.

Table 3. Changes in the Electronic States of $(CH_3)_3SCl$ and $O_2$ due to the O-O Streching. (S-Center of O-O axis=3.0 Å.)

| O-O | $(CH_3)_3SCl$, AO population | | | | | $O_2$ | | |
|---|---|---|---|---|---|---|---|---|
| (Å) | $p_z$ | $d_{xz}$ | $d_{yz}$ | $d_{xy}$ | $d_{z^2}$ | $(1\pi_g)_z$ | $(1\pi_g)_y$ | $E_{EH}$(eV)a) |
| 1.2072 | 0.5700 | 0.1504 | 0.1444 | 0.0921 | 0.0720 | -11.72 | -11.71 | -832.34 |
| 1.2696 | 0.5701 | 0.1491 | 0.1445 | 0.0921 | 0.0689 | -12.04 | -12.03 | -833.64 |
| 1.30 | 0.5703 | 0.1484 | 0.1447 | 0.0921 | 0.0675 | -12.17 | -12.16 | -834.20 |
| 1.34 | 0.5707 | 0.1474 | 0.1448 | 0.0921 | 0.0659 | -12.34 | -12.33 | -834.89 |
| $O_2$ | | | | | | -11.72 | -11.72 | -251.60 |

a) Total energy of the system calculated by the extended Hückel method, augmented by sulfur d-orbitals: coulomb integral of sulfur d-orbital was -7.00eV.

Finally, a further discussion was developed concerning the interaction mentioned above. The electrons migrated from the sulfur d-orbitals of the sulfonium compound to $O_2$ would bring about the electron repulsion in $O_2$ with the electron back-donation from $1\pi_u$-orbitals of the latter to the former. This electron repulsion accompanies the streching of the O-O. As can be seen from Table 3, the O-O streching stabilizes the system of $(CH_3)_3SCl-O_2$ and causes the electron-outflowing mainly from the sulfur $d_{xz}$ to $(1\pi_g)_z$-orbital of $O_2$, from which the electron back-donation occurrs to the sulfur $p_z$. Moreover, the energy-removement of the degenerated, half-occupied $1\pi_g$-orbitals can be expected in the above system.

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